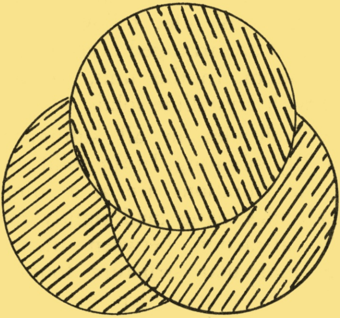
THINGS

of science



LIQUID CRYSTALS

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LIQUID CRYSTALS

It has been known since the early days of scientific history that, depending upon temperature and pressure, all matter exists in one of three states: solid, liquid or gas.

As a solid, the substance may be either crystalline or amorphous. In a crystalline compound, the molecules are arranged in an orderly fashion, in a regular three-dimensional geometric pattern characteristic of that substance. In an amorphous compound, the molecules follow no regular pattern and are arranged every which way or at random. In this unit, we are concerned with crystalline solids.

The molecules in all substances are continually vibrating. In the solid state the molecular vibrations are at a minimum, the molecules being held tightly together by the attraction between them. The orderly molecular structure found in a crystalline substance depends upon this molecular attraction.

If heat should be applied to a crystalline solid the vibrations of the molecules are increased. If the temperature is raised high enough the vibrations will become so great the molecules can no longer remain in their regular arrangement. The attraction between the individual molecules

or groups of molecules becomes so weakened the crystal structure is destroyed and the substance melts, changing into its liquid state.

In inorganic compounds the melting points are usually high because the attractive force between their components is extremely strong. But in organic compounds, the attraction between the molecules is weaker and the melting points therefore are much lower.

The change from the solid to the liquid state is specific for any compound and is usually well defined.

However, in 1888 an Austrian botanist, Frederick Reinitzer, noticed that some organic compounds showed an unusual melting phenomenon. They melted at specific temperatures but were opaque. On further heating the opacity disappeared and they became clear. This change also occurred at definite temperatures. He found that the cloudy substance, although fluid, had crystalline properties and the clear fluid was a true liquid with the molecules arranged randomly.

Compounds in this turbid state between crystal and liquid states became known as liquid crystals. This liquid crystalline state is also referred to as the mesomorphic state,

meso- meaning intermediate and morpho- meaning change in Greek.

Substances that show mesomorphism are usually organic compounds whose molecules are elongated and in some cases also flattened. Their molecular shape causes them to line up parallel with each other like a row of logs or a bundle of sticks. They exhibit the optical properties of a crystal and the fluid characteristics of a liquid.

There are two major types of liquid crystals, the thermotropic and lyotropic. Thermotropic liquid crystals pass through the states from solid, through the liquid crystalline phase, to a liquid by increases in temperature. In lyotropic liquid crystals, the changes occur due to the addition of a solvent to a comopund. The experiments in this unit deal with the thermotropic type of liquid crystals.

In the 1950's interest was revived in liquid crystals, especially in the thermotropic type and much research has been done on the subject since that time, especially on applications in the various fields of science.

Through the simple experiments in this unit, you will be able to observe the broad scope of possible ways in which liquid crystals can be utilized.

First examine your materials.

LIQUID CRYSTAL SHEET (A)—Bronze or dark brown in color depending upon the surrounding temperature—color changes occur with 25° to 35°C; 2 x 2 inches square.

LIQUID CRYSTAL SHEET (B)—Dark blue or bluish green depending upon the surrounding temperature—color changes occur within 19° to 25°C; 2 x 2 inches.

WIRE—Four inches long.

TOOTHPICK—Colored round wooden toothpick.

RUBBER BAND—Three by one-sixteenth inches.

COLORED PAPER—Two pieces; 3 x 2½ inches in size.

CHOLESTERIC LIQUID CRYSTALS

Three different types of phases in the transition of a thermotropic liquid crystal from a solid to a true liquid have been determined by their flow characteristics and optical properties. They are the smectic, nematic and cholesteric mesophases.

In general, when a substance having liquid crystalline properties is heated, it turns first into a turbid viscous fluid, the smectic mesophase. Then it becomes more

fluid, but is still cloudy, the nematic mesophase, and finally it turns clear and assumes the true liquid state. In the smectic and nematic mesophases, the crystalline structure is altered but not disorganized.

In the smectic mesophase, the molecules are parallel to each other as in the crystal state, but the compound becomes separated into layers which can slide over each other, thus allowing some movement, but not free flow. This phase is therefore viscous in nature (Fig. 1).

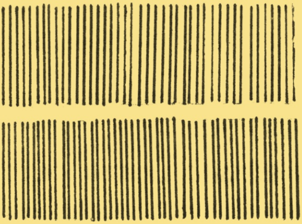


Fig. 1

The molecules in the nematic mesophase are more mobile but remain parallel to each other retaining the crystalline structure. However, the layered arrangement or stratification disappears (Fig. 2).

The smectic and nematic mesophases

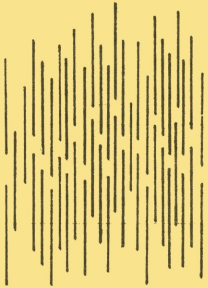


Fig. 2

are opaque or cloudy because most of the light is scattered by the molecules. In the liquid state the molecules have lost their crystalline alignment and point in every direction. Thus light can be transmitted through the spaces between the molecules and the liquid is transparent (Fig. 3).

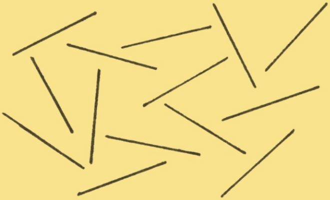


Fig. 3

The transition from solid to smectic mesophase to nematic and finally to the liquid state is well defined and reversible. The temperature at which these changes occur depends upon the nature of the compound and is independent of other compounds surrounding it.

The third mesophase, the cholesteric mesophase, is a form of the nematic mesophase. The compound is turbid and liquid in this phase, but has the unique property of iridescent color. The liquid crystal changes color with an increase in temperature. Most of the compounds exhibiting this mesophase are compounds of cholesterol.

Experiment 1. Touch the two pieces of liquid crystal sheets with the tip of your finger and note the immediate change in color that results from the warmth of your fingertip.

What causes this change in color? The optical properties depend upon the structure of the cholesteric compound.

The molecules of cholesteric liquid crystals are arranged in thin layers as are those in the smectic mesophase. However, the long axes of the molecules are parallel to the plane of the layers unlike those in the smectic mesophase which are perpendicular to the plane (Fig. 4). The

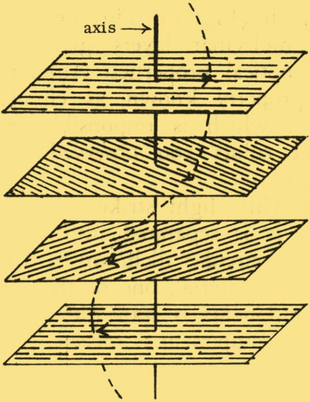


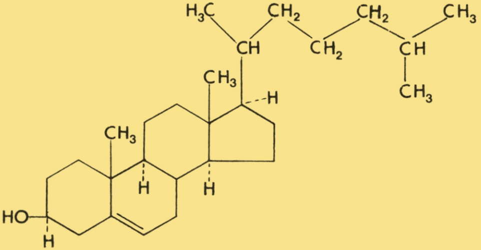
Fig. 4

parallel arrangement of the molecules within the layers is similar to the nematic mesophase.

The molecules of cholesteric compounds are flat in overall structure (Fig. 5), but some parts of the molecule may extend above or below the plane creating a corrugated-like effect. These irregularities cause the long axes of the molecules of one layer to be slightly displaced in direction from those in adjacent layers above and below. This displaced alignment of the molecules from layer to layer traces a

helical path (Fig. 4). This unique twist of the molecular layers gives rise to unusual optical properties. Among them is the property known as circular dichromism which is responsible for the iridescent colors you observed in your specimens.

When white light strikes a cholesteric material, it is separated into two components by circular dichromism. Depending on the material, one or the other of these components is transmitted and the remaining component is reflected. The re-



Molecule of cholesterol. The methyl (CH_3) groups project upward and the hydrogens (H) with dotted lines project downward from the plane of the paper.

Fig. 5

flected light is scattered and is responsible for the color of the liquid crystal.

Not all cholesteric compounds have a liquid crystal phase. Those that do, however, all have flat, broad configurations.

The particular combination of colors of a liquid crystal depends on the shape and components of the compound, the temperature, the angle at which the light strikes it (the angle of incidence) and the angle from which it is observed.

Note the black background on your sheets of liquid crystals. Cholesterol compounds do not absorb light. They transmit it or scatter it selectively. Only a small fraction of the incident light is scattered. Therefore, a black background is used to absorb the transmitted light and prevent its reflection. This helps enhance the purity of the scattered colors reflected by the liquid crystal system.

Tape one edge of each of your two specimens of liquid crystals to the 2½-inch edge of your pieces of colored paper to the depth of about ⅛ inch (Fig. 6). The paper strips will serve as holders so that you will not have to touch the specimens as you do your experiments. Write the letter A on the holder for the bronze-colored specimen and B on the holder for the bluish-green specimen. This is for

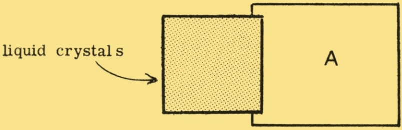


Fig. 6

easy identification and reference. [NOTE: These colors are evident if the temperature of the room is about 25°C (77°F). If either of the specimens is black, it means that the compound is in its solid state because the temperature is below that of the cholesteric mesophase for the substance. The crystals appear black because of the black background.]

The liquid crystal specimens in your unit were both prepared by the National Cash Register Company, Dayton, Ohio. The compounds were microencapsulated and mounted on transparent Mylar, then coated with a black background material.

In the microencapsulation process, the cholesteric compound is emulsified into microscopic droplets and dispersed in a medium containing a walling material, usually a transparent polymer. The walling material encloses the microscopic particles completely so that each becomes an independent package. Microencapsulation makes the liquid crystals easier to

handle and protects them from the environment, giving them a longer shelf life, without interfering with their distinctive color changes.

The bronze-colored specimen designated A is a new formulation of NCR and is called Chromatic ELC Type A. The color-play temperature has a spread of approximately 5°C in the 25° to 35°C temperature range. This comopund is very sensitive to temperature changes, reacting very quickly even to very small fluctuations. The color change includes all colors of the visible spectrum—red, orange, yellow, green, blue and violet.

Experiment 2. Place specimen A on your arm and note the transition of the colors. Do you see all the colors of the spectrum? Note the rainbow-like colors along the outer edges of the color change, showing the gradations in temperature—highest at the source (violet) and coolest at the most distant point (reddish).

You can see at once that the reaction is reversible since as soon as the source of heat is removed the colors begin to disappear.

Experiment 3. Observe the other sheet, specimen B. The compound for this liquid crystal is different from that of specimen A. It is referred to as W-619 by the com-

pany. Its color changes occur within the range of 19° to 25°C. This specimen also reflects all the wavelengths of the visible spectrum.

If you place the specimen on your arm you will see that it becomes deep violet in color. But in order to turn it red, you will have to expose it to a lower temperature. Hold it in the cold air of the refrigerator and observe the color changes. Does it show all the colors of the spectrum as it cools? What happens when you remove the specimen from the refrigerator?

Most cholesteric liquid crystals follow the sequence of colors of the solar spectrum, whether all six wavelengths are reflected or only some of them. Which wavelengths will be seen and at what temperatures is controlled by the chemical composition of the liquid crystal and its molecular structure.

Why do the colors change when the compound is warmed or cooled?

The change of color of the cholesteric mesophase with temperature is a complex function of the molecular structure. When the temperature is raised, the weak forces between the molecules of the cholesteric compound are disturbed and the molecules begin to move as the intermo-

lecular attraction is decreased. The molecular alignment becomes disarranged and the tilt of the molecules is also disturbed as they begin to flow. The structural changes cause the reflection and scattering of lights of different wavelengths and thus different colors appear. The color changes always occur, in a certain order. At a certain given temperature a particular compound will always show the same color and the rate of change from color to color always remains the same. This fact is very important in various applications of liquid crystals.

The rate at which color changes occur, the rate of thermal change, depends on the viscosity of the substance and how quickly the new arrangement of molecules can flow.

Experiment 4. Hold your fingertip on specimen A. Note how quickly the color changes occur and how rapidly they spread. Repeat with specimen B. Does the color change occur as quickly or more slowly? Do the colors spread as rapidly? The reaction of specimen A to temperature is much more sensitive than specimen B.

Cholesteric liquid crystals are made in a wide variety of temperature ranges and rates of change for specific applications.

Experiment 5. The color of a liquid crystal at a certain temperature depends also on the angle of the incident ray and the position from which it is viewed.

Hold specimen B at a certain angle and note its color. Without changing your position slowly turn the specimen so that the light strikes it at a different angle. Does its color change? Does it look more green than blue or more blue?

Now hold the specimen in one position and then view it from different directions. Does its color change?

At any temperature, the color, or the predominant wavelength, depends on the

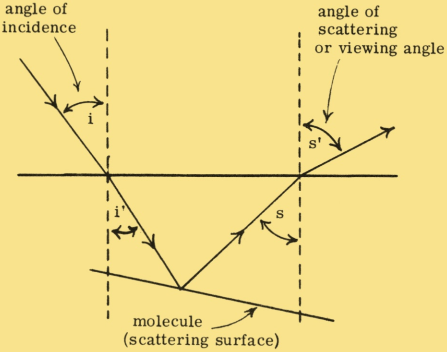


Fig. 7

angle of incidence and the angle of scattering (Fig. 7).

The iridescence you observe is similar to that produced by a thin film of oil on water.

EXPERIMENTS WITH LIQUID CRYSTALS

HEAT TRANSFER

We are all familiar with the sensation of hot and cold and the thermometers we use to measure the temperature. Because of the color changes that occur in cholesteric liquid crystals with changes in temperature, these chemicals too can be used to detect and measure heat.

Heat is a form of kinetic energy due to the motion of molecules. It can be stored, transferred or transformed from and converted into other forms of energy. The motion of the molecules resulting from heat is called thermal motion. The energy of this thermal motion can be transferred in solids, liquids and gases.

Experiment 6. Place about one inch of one end of your steel wire on specimen A and after any color changes that might have occurred because of the differences in temperature of the liquid crystals and

the wire have disappeared, hold the free end of the wire about one inch or more away from the edge of the liquid crystal sheet.

Within a very short time, you will see a gradual change in the color of the liquid crystals beneath the wire indicating that the heat from your hand has been conducted along the wire to the liquid crystals. As you continue to hold the wire note that the color will change to green and perhaps even blue. The heat energy of your hand was transferred to the liquid crystal molecules by thermal motion. Note that you can observe the gradual increase in temperature along the wire by the color changes. (Some heat, of course, is lost to the surrounding air as it is transferred along the wire.)

Experiment 7. Now allow the wire to return to room temperature and place it on sheet B in the same way. Instead of holding the wire this time, place a piece of ice wrapped in the polyethylene bag in your unit or other plastic bag on the end of the wire.

What happens? Does the sheet change color? Does the color change indicate increase or decrease in temperature?

Thermal conduction is from the warmer object to the colder. Heat from the liquid

crystals is transferred to the ice, causing the liquid crystals to decrease in temperature.

Experiment 8. Repeat Experiment 6 with the wooden toothpick in your unit. Does any color change occur in the liquid crystals? Thermal transfer in wood is extremely low, so you see no change in the color of the liquid crystals.

Most metals, like the steel wire in your unit, are good conductors of heat, while wood is a poor conductor. This explains why matches are made of wood or other cellulosic material.

Experiment 9. On a cold day when the temperature outside is about 15°C or lower, note the color of specimen B at room temperature (should be blue or blue-green). Take the specimen close to a window. Does it change color? The warm air from the room is conducted through the thin glass to the outside air. The air in a room is therefore cooler near a window than next to a wall.

Experiment 10. Energy transferred to an object by another remains until it is transferred to the surrounding air and reaches equilibrium with it.

Hold your fingers down firmly on a table for about 15 seconds. Then place specimen A over the same spot. Do you

see an imprint of your fingers in color on the sheet? The heat transferred from your fingers to the table is now transferred to the liquid crystal molecules. Note the gradual change in the color as the heat energy is transferred to the air. When thermal equilibrium is reached the imprints completely disappear.

Thermal transfer is fairly slow. This property is made use of in testing metal defects with liquid crystals. Cracks, holes and other defects on a metal plate may be shown by an increase in velocity of heat as it approaches the defect and a decrease in velocity after it has passed it by.

CONVECTION OF HEAT

When air comes in contact with a hot surface, circulation takes place automatically. This movement of the air is known as convection. In a room, although you may not notice it, the air is in constant motion influenced by a lighted lamp, body temperature, open windows and other conditions.

Experiment 11. Take sheet A and bring it down close to the floor. Note its color. Now slowly raise it toward the ceiling watching for any color changes. What do the color changes indicate?

From the reaction of the liquid crystals

you can show that the air is warmer toward the ceiling than close to the floor. The lower density of the heated air causes it to rise and when it cools its density increases and it sinks toward the floor.

Experiment 12. Take specimen A from room to room. Do you find that some rooms in your home are warmer than others?

Experiment 13. Light a single lamp in a room. Hold the liquid crystal sheet A above it and note the color change to a deep blue or violet. Now take the sheet across the room. Does the sheet change color? Even slight differences in temperature in different parts of the room can be detected by liquid crystals. One of the greatest advantages of liquid crystals is their extreme sensitivity.

Experiment 14. Hold specimen B near an air conditioner and note the color change as the cold air blows across it. Gradually move away from the air conditioner observing any changes in color in the liquid crystals. Move in different directions. Can you check the effectiveness of the air conditioner by this means?

Experiment 15. The movement of air across a surface has a cooling effect. Place specimen A in an environment of

about 80°F so that it turns green. Now fan it briskly. Does the color become reddish brown? Thermal energy is transferred to the air from the liquid crystals and carried away by the flow of air created by fanning.

Flowing liquid serves the same purpose. The heat of an automobile engine is transferred to water circulating through pipes. When the water is returned to the radiator, the revolving fan and air passing over the radiator cores as the car moves along carry away the heat energy picked up from the engine.

HEAT PRODUCTION

Experiment 16. Do this experiment in a room about 25°C so that specimen A will be bronze colored. Take your rubber band and place it across the surface of the sheet. Allow the rubber band to remain on the surface until the two are at the same temperature.

Now take opposite ends of the rubber band with each hand and keeping it in close contact with the surface stretch it quickly. Look at the surface beneath the rubber band. Are there two streaks of green? The work of sudden stretching and the friction between the molecules

as they are pulled apart release energy in the form of heat.

Now, with the rubber band still stretched, allow it to rest on the surface again. Now permit it to shrink to its original size. Quickly look beneath it. Are there two black streaks? When the rubber band shrinks it absorbs heat from its environment regaining the energy it lost on stretching, thus reducing the temperature of the liquid crystals.

Experiment 17. Rub your toothpick briskly back and forth across the surface of this page for a minute or so, then place the rubbed side on specimen A. What happens? Does your result show that heat was generated? As with the rubber band, friction and work were converted into heat energy.

Experiment 18. Bend your wire in half and then bend it back and forth rapidly for a number of times. Touch the bent area to the surface of specimen A. Do you see a color change? Friction and work again are responsible for the heat released.

Experiment 19. With a pencil draw a small O about an inch high on a piece of paper bearing down heavily and going over the letter several times. Immediately place specimen A over the O. Do you

obtain an image of the letter on the sheet? The friction of your pencil and the work involved in writing were converted into heat.

Experiment 20. Take specimen A and place it over an electric wire leading to a lighted lamp. Does a color change occur? The resistance in the electric wire that an electrical current must overcome produces heat.

HEAT ABSORPTION

Experiment 21. Dissolve a half a teaspoon of baking soda in a teaspoon of water in a thin glass or vial. Place the container on specimen B. Add to the solution a teaspoon of vinegar, then look under the container. Does the color change show that this chemical reaction absorbed heat?

Experiment 22. Place a small drop of water on specimen B. Watch for any color changes. Does it turn green or yellow? When water evaporates it absorbs the heat needed to change into the vapor state.

Experiment 23. Wrap the tip of your toothpick in a small piece of cotton or tissue and then dip it into some rubbing alcohol. Now, trace your initial on the surface of specimen B with the wet point.

Note the spectacular color change. Alcohol evaporates rapidly and absorbs much more energy than water does as it changes into the vapor state.

BODY TEMPERATURE

Experiment 24. Hold your hand about one-half inch above the liquid crystal specimen A. Note the gradual color change. The heat radiated by your body is registered by the liquid crystals.

Experiment 25. Place the liquid crystal on your arm and note the quick color change to dark blue or violet.

Liquid crystals are used to observe differences in temperature in the skin in different parts of the body. Cholesteric liquid crystals are used by doctors to discover diseased areas by temperature. This technique is called thermography. This method permits immediate visual observation of the surface temperature in color and the findings can be reproduced by photography. The procedure is simple and inexpensive, but should be done only by licensed medical doctors who are able to properly interpret the color patterns.

Experiment 26. If you have a houseplant, hold specimen A or B close to it. Do any color changes occur? If so, can you explain your results?

You have observed the sensitivity of liquid crystals to small temperature variations. This characteristic makes them useful for various applications including non-destructive testing. They are utilized in thermal testing problems in the aerospace industry and are especially useful in areas where complicated instruments would otherwise be needed.

A technique known as thermal mapping like that used on human skin is used to check such things as the flow of a coolant to see whether or not a blockage exists; locate shorts; and observe the uniformity of resistance heating of aircraft windshields.

As your experiment with the wire showed, the presence of strain on metals can be detected by the heat generated. A growing fatigue crack may be located by noting temperature deviations.

From your experiments you can see the wide variety of possible applications of liquid crystals in medicine, engineering, biology, electronics, and other fields of science. Liquid crystals find application also in toys, clocks and novelties, as well as in art.

We have only touched on this interesting field of chemistry and you may wish to pursue the subject further. The refer-

ences below will be helpful.

Chemical Reviews, Volume 57, No. 6, Dec. 1957, Published by the American Chemical Society.

Liquid Crystals, Glenn H. Brown, G. J. Dienes, M. M. Labes, Gordon and Breach, Science Publishers, New York, 1968.

Molecular Structure and the Properties of Liquid Crystals, G. W. Gray, Academic Press, New York, 1969.

Appreciation is expressed to the National Cash Register Company for their cooperation in producing this unit, and to the Diamond National Corporation, New York, which contributed the toothpicks.

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